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# INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)


(51) International Patent Classification 6 : C22C 19/05, F22B 37/04

A1

(11) International Publication Number: WO 95/31579

(43) International Publication Date: 23 November 1995 (23.11.95)

(21) International Application Number: PCT/SE95/00561

(22) International Filing Date: 17 May 1995 (17.05.95)

(30) Priority Data:
9401695-3 18 May 1994 (18.05.94) SE



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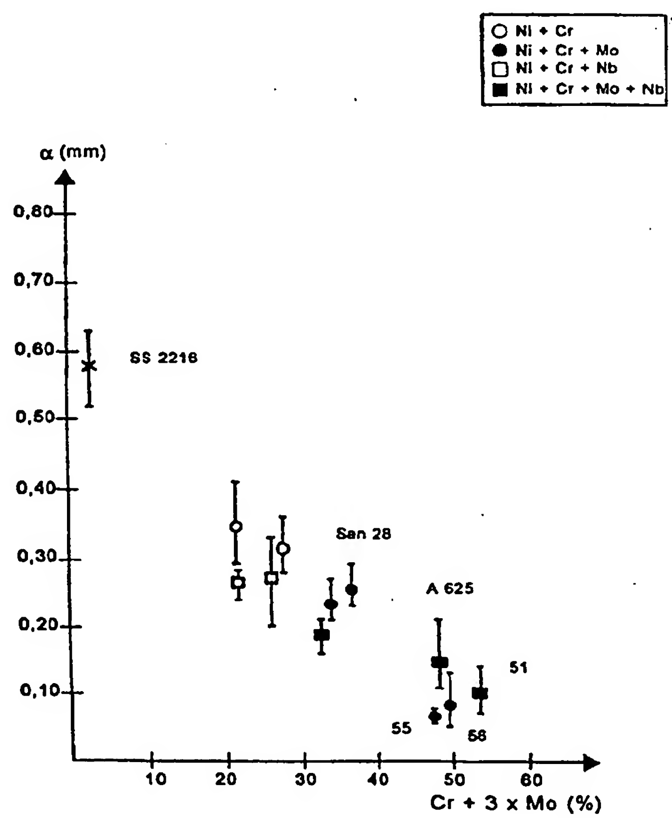
(81) Designated States: CA, FI, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

**Published**
*With international search report.*


(54) Title: AUSTENITIC Ni-BASED ALLOY WITH HIGH CORROSION RESISTANCE, GOOD WORKABILITY AND STRUCTURE STABILITY

## (57) Abstract


The invention provides an austenitic Ni-based alloy with improved workability, good corrosion resistance and good structure stability preferably for usage as tube material in sulphur-, chloride- or alkaline-containing environments. The material has an austenitic structure which contains in weight % up to 0.025 C, 20-27 Cr, 8-12 Mo, up to 0.5 Si, up to 0.5 Mn, up to 0.3 Al, up to 0.1 N, 3-15 Fe, up to 0.5 Ti, up to 0.5 Nb, the remainder being Ni and usual impurities.

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Austenitic Ni-based alloy with high corrosion resistance, good workability and structure stability

The present invention relates to an austenitic Ni-based alloy useful as construction material that satisfies demands in regard of high corrosion resistance, good hot workability, good tensile strength and structure stability.

Normally low alloyed steels are used in waste incineration boilers. It is a well known problem that large corrosion problems occur in such furnaces. It is a normal method primarily in USA to protect this low alloyed material by overlay-welding a highly alloyed layer of a material such as A 625 which has been found to reduce the corrosion problems considerably. Overlay-welding like this is not practically useful for tubes that are not used as panels such as super-heaters. As alternative means instead of overlay-welding is the usage of composite tubes in which A 625 is used as an external layer. This should result in a good product from corrosive aspect, however, such tubes are difficult to manufacture due to the large deformation forces that needs to be used in hot working. The material is furthermore sensitive for crack formation during cold working.

It is a complex optimization to provide an Ni-based alloyed material with good corrosion resistance and simultaneously good workability. However, by carrying out a systematic development work it has now been possible to provide a Ni-based alloy material that in a surprising manner can bring optimal properties in regard of corrosion resistance combined with hot

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workability, tensile strength and structure stability. By achieving these material properties such material becomes useful not only as an external component in tubes for waste combustion furnaces but also as material in black liquor recovery boilers, coal gasification etc.

The invention comprises the usage of a Ni-based alloy with austenitic micro-structure containing, in weight-%:

| | | |
|---|---|---|
| C | up to | 0.025 % |
| Cr | | 20-27 |
| Mo | | 8-12 |
| N | up to | 0.10 |
| Fe | | 3-15 |
| Ti | up to | 0.5 |
| Nb | " | 0.5 |
| Si | " | 0.5 |
| Mn | " | 0.5 |
| Al | " | 0.3 |
| Ni | remainder (except normal impurities) | |

whereby the contents of the various constituents are such that following condition is fulfilled

$45 \leq Cr + 3 \times Mo \leq 57$.

In parallel, also the condition $\frac{Ti}{N} \geq 1.5$ ought to be fulfilled, where Ti and N are given in weight-%.

Further details and advantages of the present invention will appear from the following description of an extensive test program that has been carried out.

Bar samples were made out of selected test alloys. The manufacture included ingot casting, extrusion and heat treatment. During extrusion the alloys were subjected to a reduction of diameter from 77 mm to 38 mm. Test

samples were taken out of each bar, subjected to hot workability testing (Gleeble) tensile strength testing, thermal analysis and corrosion testing in a full scale plant for waste incineration. These tests have also been followed by real installation of tubes made of Sanicro 28 and A 625.

Table 1 below shows the chemical analysis of the investigated test alloys which have been subjected to all the three above mentioned test procedures. The first alloy in Table 1 is designated SS 2216 which is a low alloy superheater steel corresponding to international standard ASTM SA213-T12. The second alloy is one of our developed and marketed alloy called Sanicro 28 which corresponds with international designation UNS 08028. The third alloy is an alloy bought on the market called A 625 with international designation UNS 06625. The alloys following thereafter in the table are test alloys made for this investigation, in the following only identifiable by the two last digits. The analysis of these test alloys has been varied such that the impact of Fe, Cr, Ni, Nb and Mo can be studied more closely.

Table 1

| | C | Si | Mn | Ti | Al | N | Cr | Ni | Mo | Nb | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|
| SS 2216 | 0,12 | 0,25 | 0,50 | - | - | - | 0,95 | - | 0,55 | - | 97,5 |
| Sanicro 28 | 0,01 | 0,45 | 1,7 | - | - | 0,03 | 26,7 | 30,6 | 3,3 | - | 37,1 |
| A 625 | 0,036 | 0,11 | 0,32 | 0,34 | 0,22 | 0,013 | 21,8 | 61,2 | 8,8 | 3,8 | 2,8 |
| Sanicro 63X51 | 0,028 | 0,20 | 0,27 | 0,26 | 0,15 | 0,020 | 32,0 | 51,6 | 7,2 | 2,1 | 6,2 |
| Sanicro 63X52 | 0,029 | 0,19 | 0,23 | 0,28 | 0,24 | 0,008 | 11,5 | 72,3 | 7,0 | 2,1 | 6,0 |
| Sanicro 63X53 | 0,033 | 0,22 | 0,26 | 0,34 | 0,27 | 0,016 | 21,8 | 62,7 | - | 3,7 | 10,7 |
| Sanicro 63X54 | 0,030 | 0,22 | 0,26 | 0,31 | 0,24 | 0,007 | 26,1 | 65,9 | - | 3,8 | 3,1 |
| Sanicro 63X55 | 0,030 | 0,21 | 0,27 | 0,29 | 0,20 | 0,008 | 21,8 | 62,8 | 8,6 | - | 6,2 |
| Sanicro 63X56 | 0,029 | 0,23 | 0,27 | 0,29 | 0,19 | 0,008 | 23,7 | 63,8 | 8,6 | - | 2,7 |
| Sanicro 63X57 | 0,031 | 0,23 | 0,26 | 0,32 | 0,22 | 0,005 | 21,6 | 63,0 | - | - | 14,3 |
| Sanicro 63X58 | 0,029 | 0,27 | 0,23 | 0,30 | 0,18 | 0,007 | 27,7 | 68,5 | - | - | 2,7 |
| Sanicro 63X59 | 0,029 | 0,24 | 0,25 | 0,32 | 0,20 | 0,011 | 22,1 | 61,6 | 4,0 | - | 11,1 |

The corrosion tests were carried out by mounting the various alloys on a cooled testing probe. These probes were thereafter located in the superheater section in one of the waste incinerators. The probe testing was done at material temperatures of 450°C during 90 days and 500°C during 45 days, althogether in four test runs, and the average loss of material $\alpha$ (mm) was measured, based on eight crossections around the samples circumference. The internal corrosion attacks were found to be negligible. The results from 500°C testing is shown in Fig. 1.

The following conclusions were made:
Nb, Fe and Ni gave no significant effect on corrosion rate within the studied alloy range. Cr and Mo give a positive effect on the corrosion rate, and alloys 51, 55 and 56 are at least comparable with alloy A 625 from corrosive point of view. Other test alloys gave results worse than A 625 regarding corrosion rate.

A careful analysis of the corrosive data from probe testing of these alloys shows a proportional relation between Cr + 3 x Mo and corrosion rate ß. This means that $ß = -k_1 \times (Cr + 3 \times Mo) + k_2$. An increase of Cr + 3 x Mo gives an almost linear reduction in corrosion rate.

In order to investigate the corrosion resistance sond samples in the form of rings were manufactured out of the extruded bar from the test alloys. The results are shown in Table 2. Large differences in hot workability were observed, during extrusion.

Table 2

| Alloy | Max-force (bar) | Appearance |
|---|---|---|
| 51 | 120 | Many surface cracks |
| 52 | 130 | "- |
| 53 | 115 | "- |
| 54 | 110 | "- |
| 55 | 130 | A few surface cracks |
| 56 | 130 | "- |
| 57 | 95 | Minor surface cracks |
| 58 | 100 | "- |
| 59 | 110 | "- |

Extrusion temperature was in all cases 1130°C.

From the above it appears that Nb has a negative effect on hot workability as regards crack formation. It also appears that Mo, to a certain extent, will increase the deformation force needed. Inspection of the material after extrusion has shown that the Nb-alloyed variants 51, 52, 53 and 54 appeared to have a larger number and more deep surface cracks than those alloys that are not alloyed with Nb.

In order to provide a larger amount of test alloys for the testing of hot workability and strength the number of alloys was increased, beyond those in Table 1, to include also those in Table 3 below.

Table 3

| | C | Si | Mn | Ti | Al | N | Cr | Ni | Mo | Nb | Fe | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sanicro 63X61 | 0,007 | 0,31 | 0,30 | 0,26 | 0,15 | 0,038 | 25,6 | 55,3 | 6,1 | - | 9,8 | 2,0 |
| Sanicro 63X62 | 0,005 | 0,42 | 0,34 | 0,21 | 0,10 | 0,034 | 29,6 | 53,1 | 6,2 | - | 10,1 | - |
| Sanicro 63X63 | 0,005 | 0,33 | 0,29 | 0,22 | 0,15 | 0,022 | 25,5 | 53,6 | 10,1 | - | 9,9 | - |
| Sanicro 63X64 | 0,008 | 0,29 | 0,31 | 0,24 | 0,14 | 0,018 | 20,5 | 56,5 | 12,2 | - | 9,8 | - |
| Sanicro 63X65 | 0,007 | 0,32 | 0,30 | 0,24 | 0,15 | 0,023 | 25,4 | 51,7 | 12,2 | - | 9,7 | - |
| Sanicro 63X66 | 0,008 | 0,32 | 0,30 | 0,23 | 0,13 | 0,012 | 15,2 | 58,5 | 15,0 | - | 10,1 | - |

Hot workability testing (Gleeble) was carried out on all alloys, i.e. Sanicro 28, A 625 and alloys 51-59 and 61-66.

As a basis for studying the force needed for the forming at high temperatures Gleeble-curves such as shown in Fig. 2 were produced where a temperature marking has been made at 50 % ductility ($T_1$) and one at the maximum ductility ($T_2$). The force is measured along the Gleeble-curve at positions $T_1$ and $T_2$. A straight line is drawn between these two points. This is illustrated in Fig. 3. What appears from Fig. 3 is an essential reduction of the force needed for the alloys that do not contain any Nb in comparison with A 625. The reduction of force due to the exclusion of Nb is largely associated with an increase of solidus temperature and upper hot working limit which enables hot-working to occur at a higher temperature where the deformation resistance is lower. Fig. 4 shows maximum deformation force $F_{max}$ (kN) at maximum ductility.

Fig. 5 shows solidus- and liquidus lines for alloys 51-59 and 61-66. For the alloys that are not alloyed with Nb a correlation can be seen between these temperatures and the value Cr + 3 x Mo. By experience it is desirable from working perspective to keep solidus temperature above 1300°C. Fig. 6 shows the upper hot working limit from Gleeble-testing and defined as the temperature at which ductility approaches down to 0 %. Also here a correlation can be seen between the upper hot working limit and Cr + 3 x Mo for the alloys that are not containing any Nb. Both Fig. 4 and Fig. 5 show the unfavorable effect of adding Nb from workability point of view. Compare

also alloys 53 and 54 with 57 and 58.

Fig. 7 shows the effect of Mo and Nb upon the contraction $Z_{max}$ (%). It appears therefrom that Mo- and Nb-contents have a negative effect on ductility. Also in this case the correlation to Cr + 3 x Mo can be seen for the alloys that do not contain any Nb.

Hence, the tests that were carried show that Nb has a negative effect on the upper hot working limit and also upon maximum ductility. Mo has same negative effect upon ductility but essentially smaller effect on the upper hot working limit than Nb.

Tensile strength testing has been carried out on Sanicro 63X51-59 and 61-66. Ultimate strength $R_m$ and yield strength $R_{p\,0.2}$ are illustrated in Fig. 8. The following condition is valid for the alloy variants that do not contain Nb.

$R_m \approx Cr + 3 \times Mo$, where $R_m$ is ultimate strength (MPa)
$R_{p\,0.2} \approx Cr + 3 \times Mo$, where $R_{p\,0.2}$ is yield strength (at a remaining elongation of 0.2 %).

It also appears that the materials with Nb have higher values for $R_{p\,0.2}$ and $R_m$ at the same value for Cr + 3 x Mo. In other words, at a given value for Cr + 3 x Mo the value for $R_{p\,0.2}$ is higher when adding Nb. A lower value for $R_{p\,0.2}$ is of advantage for cold working.

In Fig. 9 measured contraction Z (%) is shown as a function of Cr + 3 x Mo. A remarkable difference appears between alloys with Nb as compared with alloys

without Nb. In the test alloys without Nb an essential reduction of grain boundary precipitations has been observed. This is related to the fact that Nb (C, N) is not formed. These could during heat treatment give additional precipitation and form a large volume fraction of $Nb_6$ (C, N). Hence, alloys without Nb give a significant reduction of unstable grain boundary precipitations which indicates that very good structure stability has been achieved.

From these observations it appears that it is advantageous if Nb is not present in the alloy since it gives no positive effect upon corrosion properties but rather a negative effect on primarily hot workability. The further conclusion that can be drawn is that it is more favorable from corrosion resistance point of view to maximize value for Cr + 3 x Mo whereas it is of advantage from hot workability point of view to minimize Cr + 3 x Mo. An optimum analysis from manufacturing and corrosion perspectives is achieved by defining the condition $45 \leq Cr + 3 \times Mo \leq 57$. At the same time the Nb-content ought to be max 0.5 %. The content of Si should preferably be selected within the range 0.20-0.40 %.

In order to find an analysis that is balanced from structure stability perspective the content of C should be max 0.025 % and the content of Fe should be 3-15 %, preferably 3-12 % and more preferably 4-8 %. At the same time the amounts of Ti and N should be selected such that the condition $\frac{Ti}{N} \geq 1.5$ is fulfilled.

The demand for C, Ti and N is related to the tendency for precipitation. The content of Fe should be

maximized to 15 %, preferably to 12 % in order to obtain good stability towards sigma phase formation.

The Cr-content should preferably be 20-24 % and Mo-content should preferably be 8-10 %. Other elements should be present in amounts less than 0.5 %.

Such an alloy has optimum properties with regard to corrosion in relation to hot workability, tensile strength and good structure stability. The analysis such as outlined above results in a material that from workability point of view is much better than A 625 but equally comparable from corrosive point of view.

In view thereof this material will be suitable for use in heat exchanger tubes in power boilers which are exposed to sulphur, chloride or alkaline containing environments which could result in high temperature corrosion.

Preferable applications include usage as superheater tubes and boiler tubes in power boilers for municipal and industrial waste incineration.

The material is well suitable for use in heat exchangers used at material temperatures of 300-550°C which are exposed to high temperature corrosion. In a preferred embodiment the material of this invention is used as material in the outer layer of a composite tube consisting of two tube components metallurgically bonded to each other by co-extrusion where the inner component consists of a conventional carbon steel (such as SA210-A1) or a low alloy pressure vessel steel (SA213-T22).

It is to be understood that, as an alternative, mono-tubes could be made of this Ni-based alloy for the purpose of being used in the above defined application areas.

Claims

1. Austenitic Ni-based alloy with good workability, good corrosion resistance and good structure stability, c h a r a c t e r i z e d in that it contains, in weight-%,

| | | |
|---|---|---|
| C | up to | 0.025 % |
| Cr | | 20-27 % |
| Mo | | 8-12 % |
| Si | up to | 0.5 % |
| Mn | "- | 0.5 % |
| Al | "- | 0.3 % |
| N | "- | 0.1 % |
| Fe | | 3-15 % |
| Ti | up to | 0.5 % |
| Nb | "- | 0.5 % |

Ni, remainder, and usual impurities, whereby the contents of the constituents are selected such that the following condition is fulfilled

$$45 \leq Cr + 3 \times Mo \leq 57$$

2. Alloy as defined in claim 1, c h a r a c t e r i z e d in that the amounts of Ti and Ni are selected such that the condition $\frac{Ti}{N} \geq 1.5$ is fulfilled.

3. Alloy as defined in claim 1, c h a r a c t e r i z e d in that the Fe-content is 3-12 %, preferably 4-8 %.

4. Alloy as defined in claim 1, c h a r a c t e r i z e d in that the Si-content is 0.20-0.40 %.

5. Alloy as defined in claim 1, c h a r a c t e r i z e d in that the Mo-content is 8-10 %.

6. Alloy as defined in claim 1, c h a r a c t e r i z e d in that the Cr-content is 20-24 %.

7. In a heat exchanger unit intended to be exposed to sulphur-, chloride- or alkaline-containing environments at high temperatures, the improvement comprising using tubes of the Ni-based alloy defined in claim 1.

8. The use of superheater and boiler tubes in a power boiler for municipal and industrial waste incinerators, the improvement comprising the use of tubes made of a Ni-based alloy as defined in claim 1.

9. In a heat exchanger unit, according to claim 8, the improvement comprising the use of said Ni-based alloy in tubes exposed to elevated temperature of 300-550°C.

10. The use of a Ni-based alloy as defined in claim 1, the improvement comprising the use of a composite tube made of two components metallurgically bonded to each other by co-extrusion, the inner portion being a conventional pressure vessel steel and an outer portion of said austenitic Ni-based alloy in the application areas defined in any of the claims 7-9.

11. The use of a Ni-based alloy as defined in claim 1, the improvement comprising the use of a mono-tube made of said Ni-based alloy for the application areas defined in claim 7-9.

Fig 1.

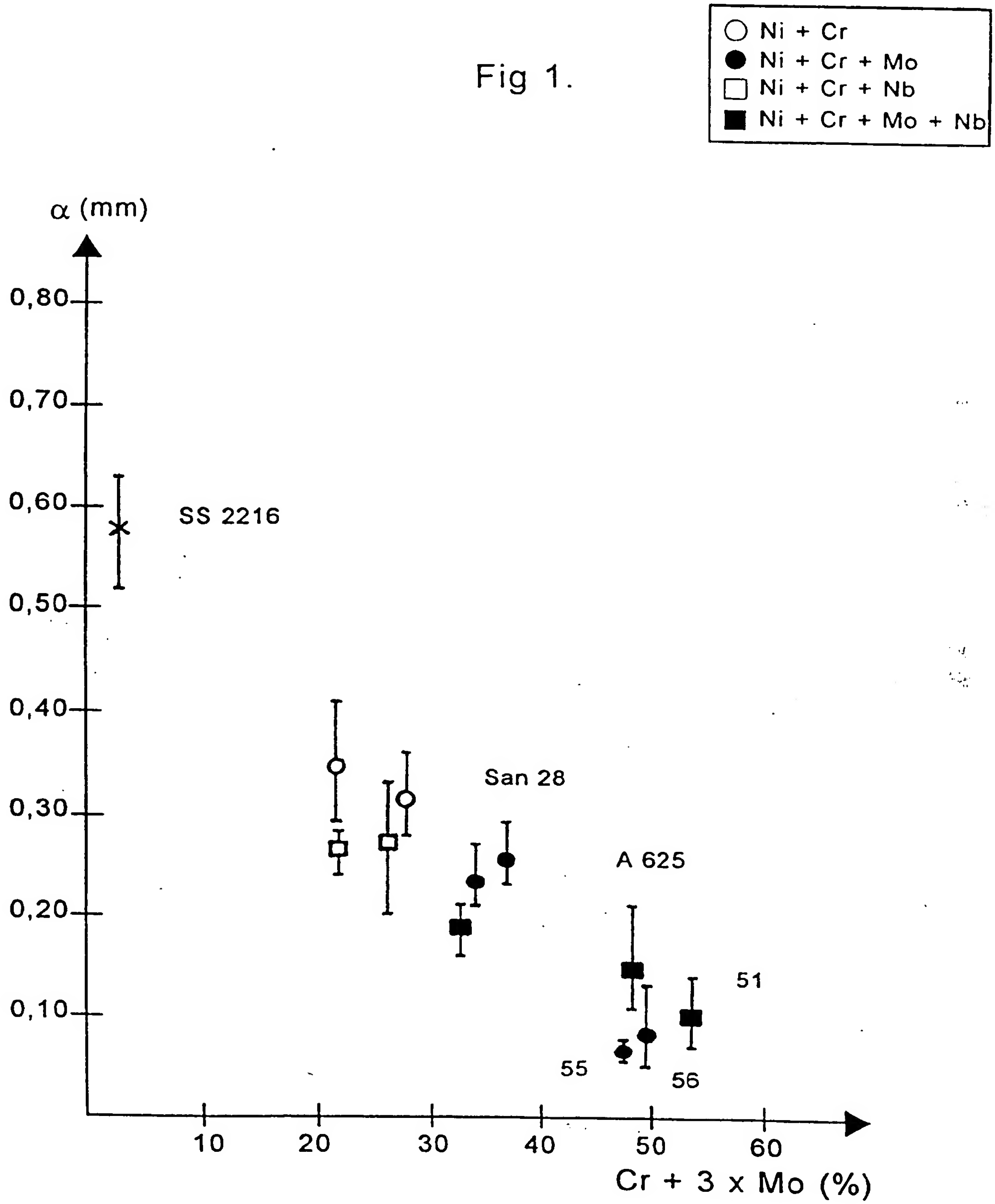


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Fig 2.

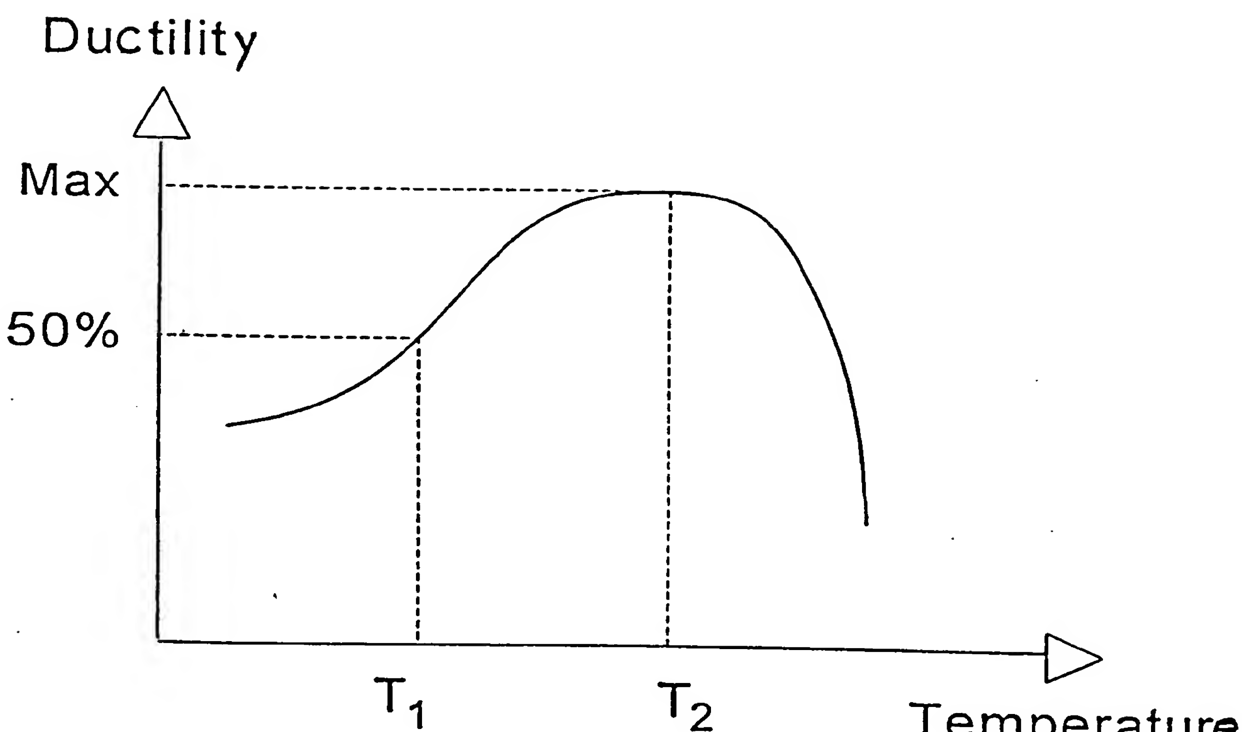

Fig 3.

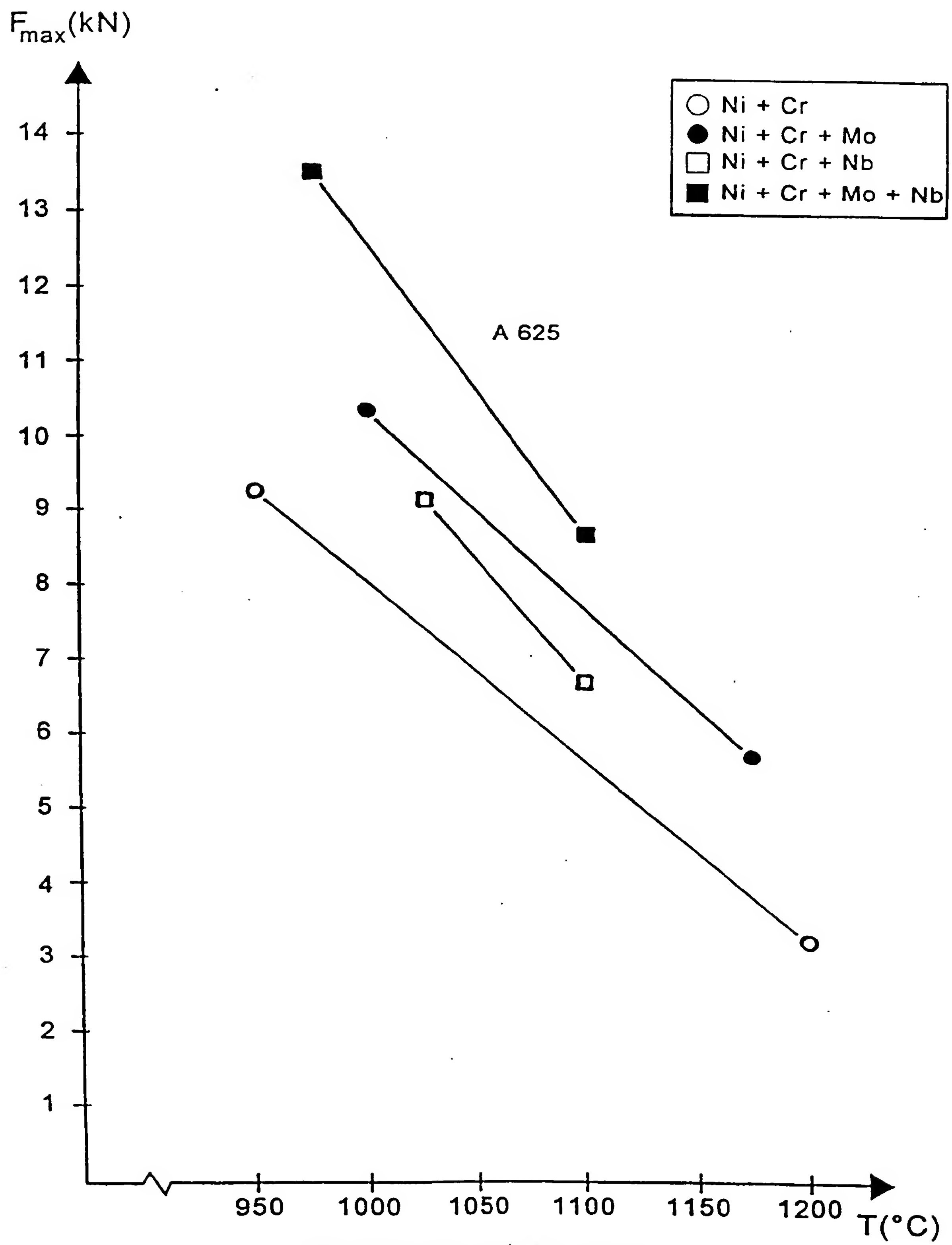


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Fig 4.

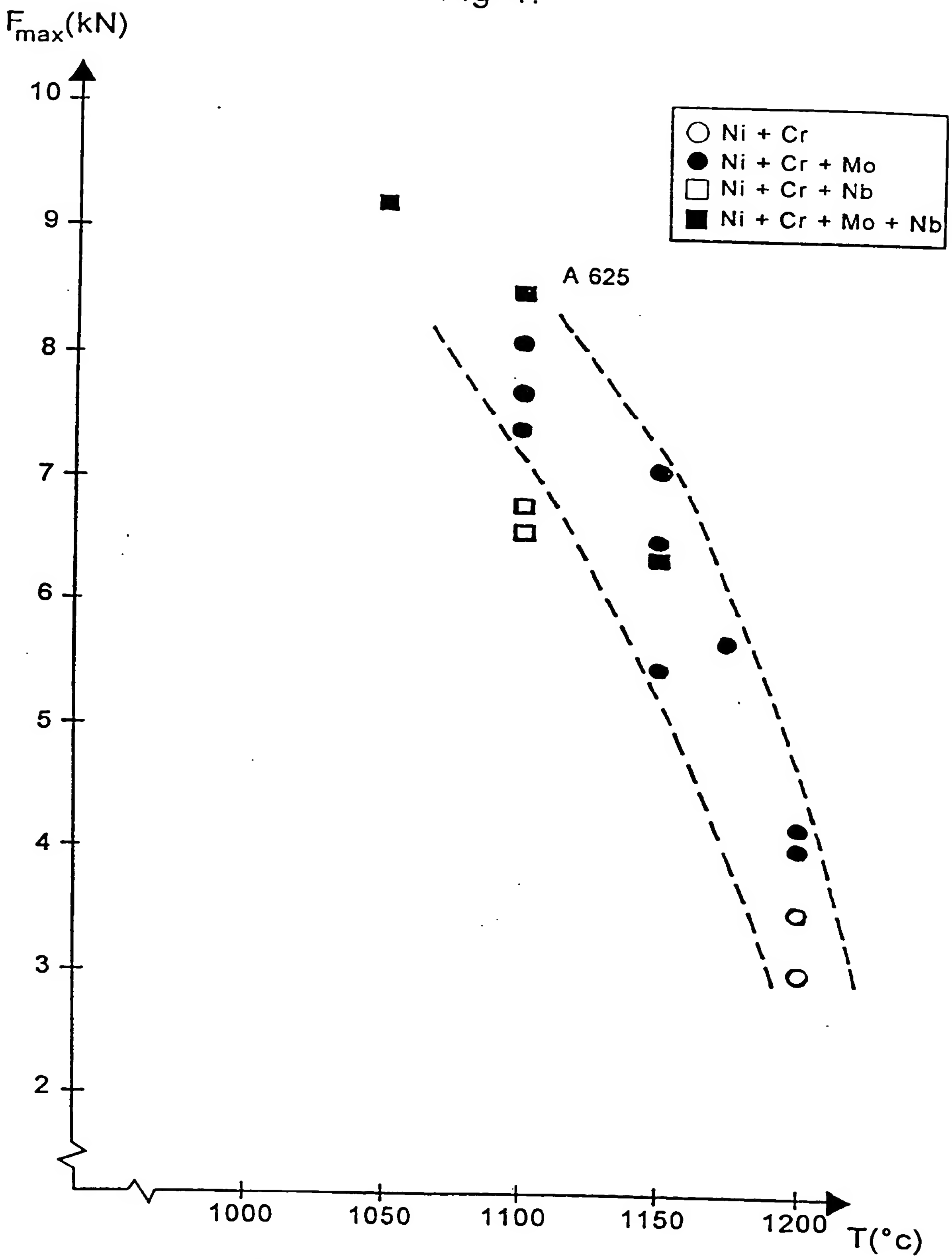
$F_{max}$(kN)
10
9
8
7
6
5
4
3
2
Ni + Cr
Ni + Cr + Mo
Ni + Cr + Nb
Ni + Cr + Mo + Nb
A 625
1000
1050
1100
1150
1200
T(°c)

Fig 7.

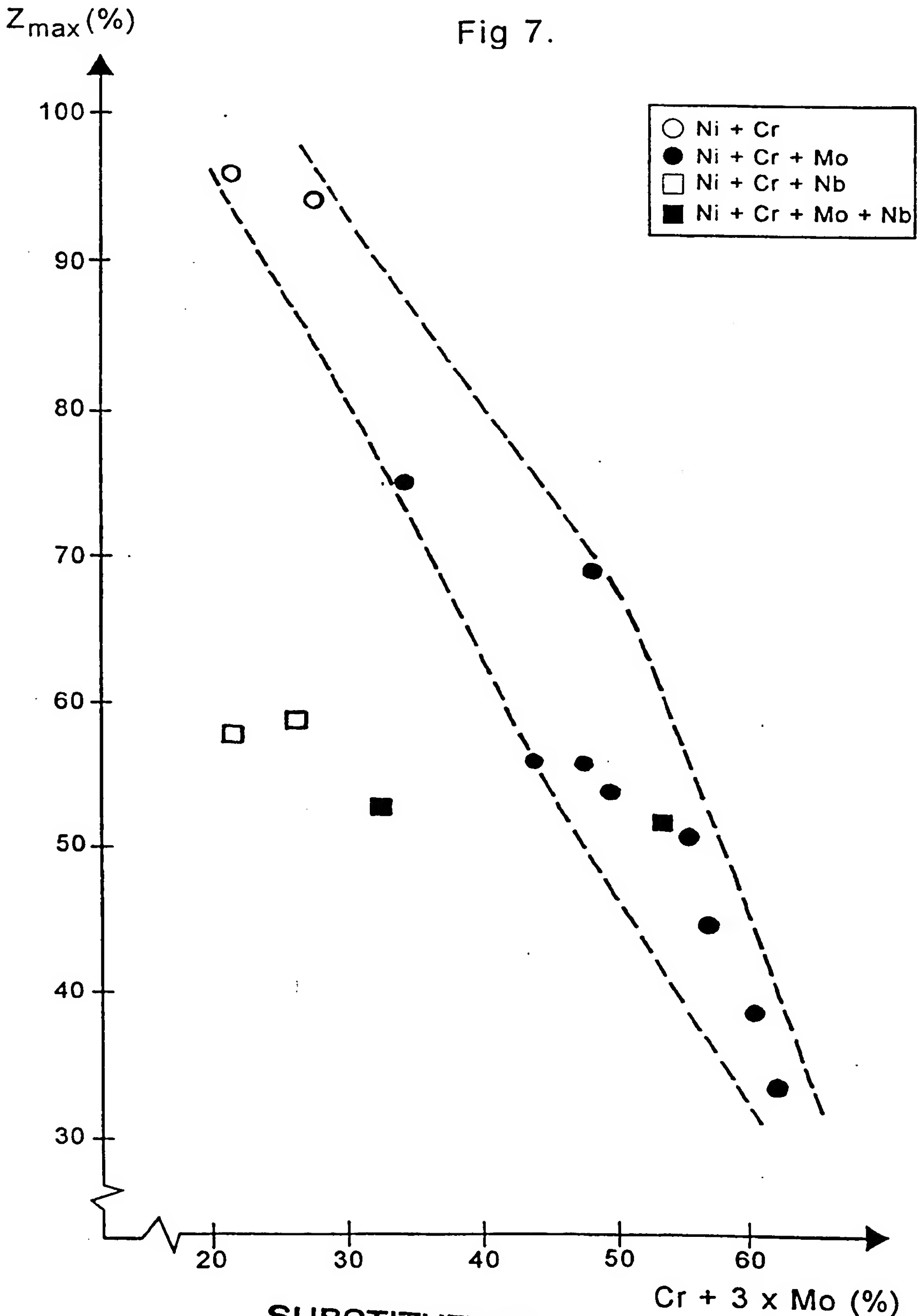
$Z_{max}$ (%)
100
90
80
70
60
50
40
30
20
30
40
50
60
Cr + 3 x Mo (%)
Ni + Cr
Ni + Cr + Mo
Ni + Cr + Nb
Ni + Cr + Mo + Nb

Fig 8.

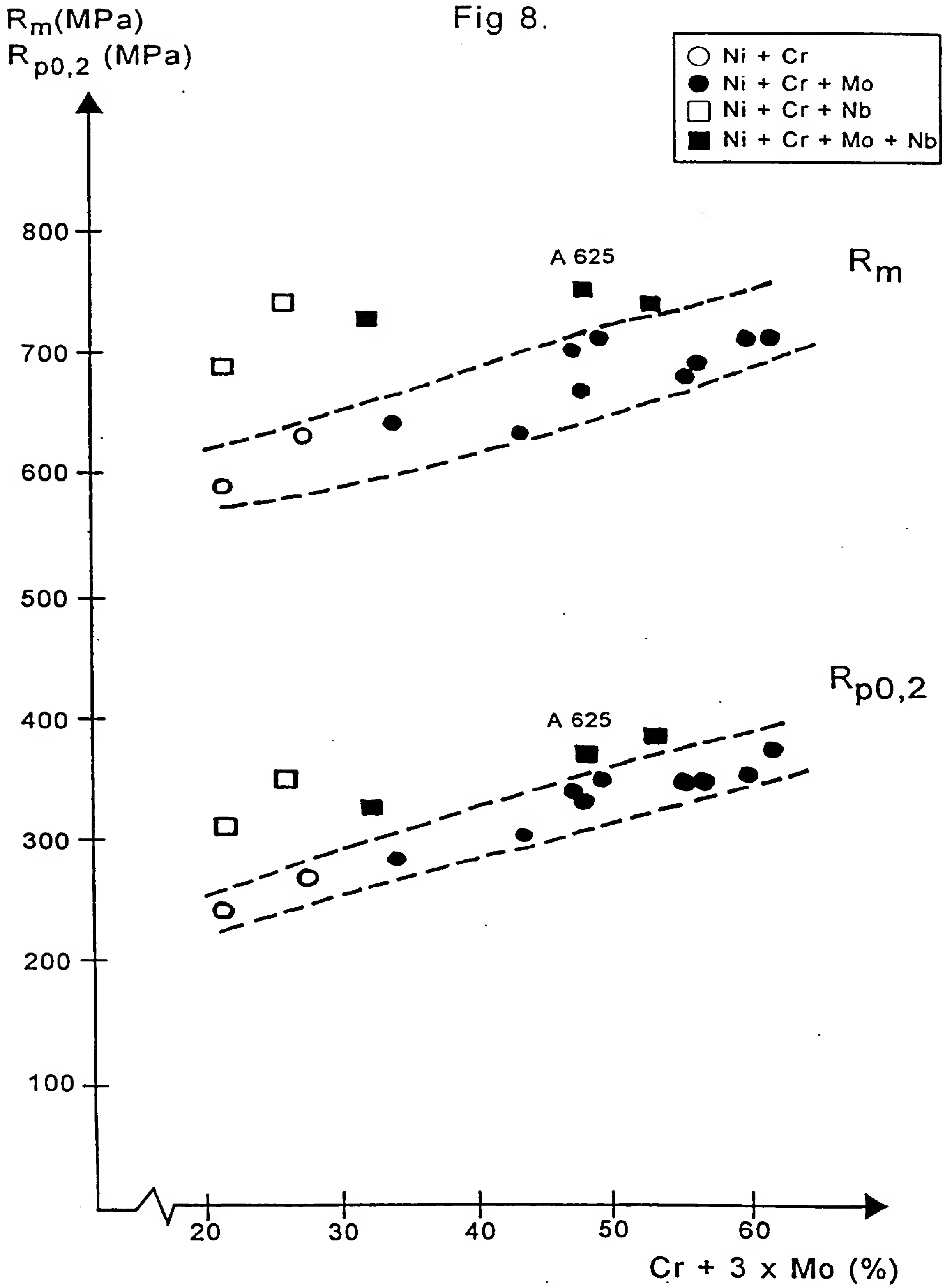


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Fig 9.

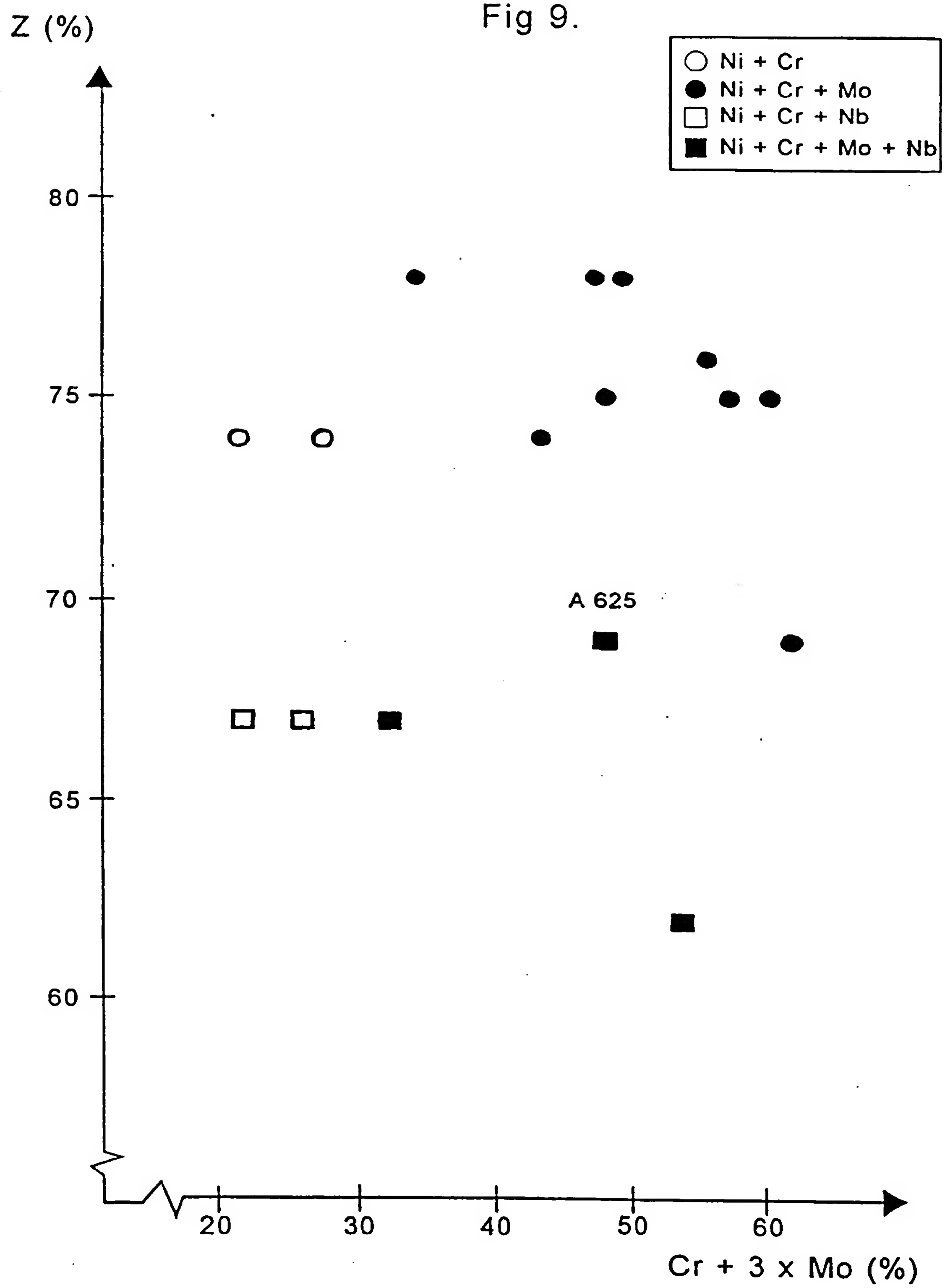

Z (%)
Ni + Cr
Ni + Cr + Mo
Ni + Cr + Nb
Ni + Cr + Mo + Nb
80
75
70
65
60
A 625
20
30
40
50
60
Cr + 3 x Mo (%)

Fig 5.

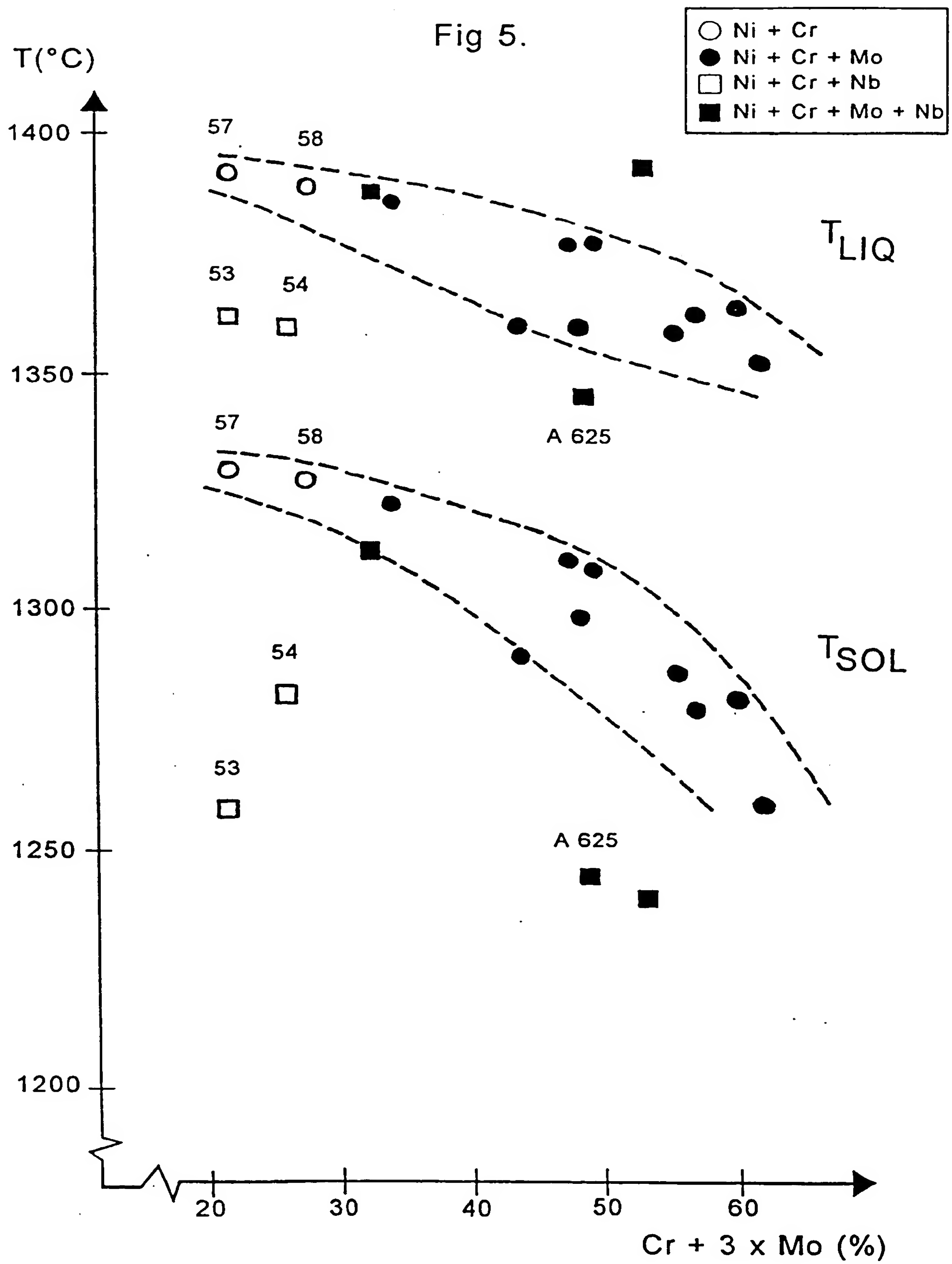
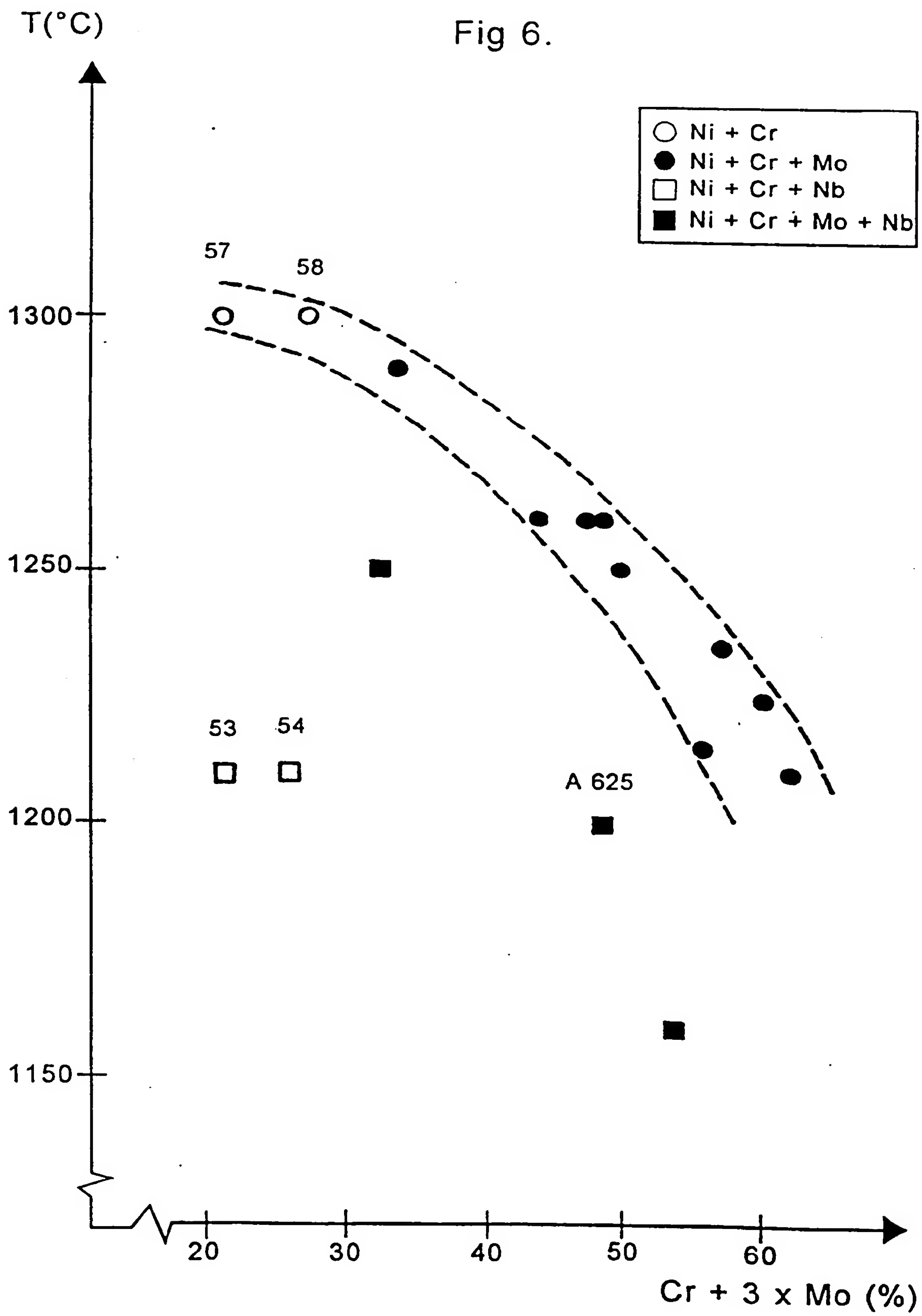

Ni + Cr
Ni + Cr + Mo
Ni + Cr + Nb
Ni + Cr + Mo + Nb
T(°C)
1400
1350
1300
1250
1200
57
58
53
54
A 625
$T_{LIQ}$
$T_{SOL}$
20
30
40
50
60
Cr + 3 x Mo (%)

Fig 6.


T(°C)
Ni + Cr
Ni + Cr + Mo
Ni + Cr + Nb
Ni + Cr + Mo + Nb
57
58
53
54
A 625
1300
1250
1200
1150
20
30
40
50
60
Cr + 3 x Mo (%)

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 95/00561

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC6: C22C 19/05, F22B 37/04
According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

METADEX

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | GB 2102834 A (SUMITOMO METAL INDUSTRIES LTD.), 9 February 1983 (09.02.83), page 2, line 50 - page 5, line 26, the tables I,III,IV,V | 1-6 |
| Y | page 1, line 1 - line 34; page 2, line 50 - page 5, line 26 | 7-11 |
| | -- | |
| X | GB 2104100 A (SUMITOMO METAL INDUSTRIES LTD.), 2 March 1983 (02.03.83), page 4, line 19 - page 6, line 51, the tables 5,9,11,17 | 1-6 |
| Y | page 1, line 1 - line 34; page 4, line 19 - page 6, line 51 | 7-11 |
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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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|---|---|
| 1 Sept 1995 | 08-09-1995 |

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# INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 95/00561

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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